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<b>(21) International Application Number:</b> PCT/US94/13707 <b>(22) International Filing Date:</b> 2 December 1994 (02.12.94)  <b>(30) Priority Data:</b> 08/163,652                      6 December 1993 (06.12.93)      US 08/330,267                      27 October 1994 (27.10.94)      US  <b>(71) Applicant:</b> WHITE EAGLE INTERNATIONAL TECHNOLOGIES, L.P. [US/US]; Suite 26C, 117 East 57th Street, New York, NY 10022 (US).  <b>(72) Inventor:</b> ROZHKOV, Igor (deceased).  <b>(74) Agent:</b> HARBST, John, W.; Rudnick & Wolfe, Suite 1800, 203 North LaSalle Street, Chicago, IL 60601-1293 (US).		<b>(81) Designated States:</b> AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PROCESS FOR PREPARATION OF HIGH TEMPERATURE COMPOSITE CERAMIC MATERIALS AND COATING		
<b>(57) Abstract</b>  Alkoxy technology is used to prepare composite ceramic materials. The starting compounds for the composite ceramic materials comprise metal alcoholates. The starting alcoholates are prepared by electrode dissolution of metals in a corresponding alcohol in the presence of an electroconductive additive. Such preparation is ecologically safe with no by products other than hydrogen, allows complete regeneration of the electroconductive additive and solvent, and can be continuous or cyclic. A broad range of metal alcoholates can be prepared using the same equipment. Raw composites are prepared with the metal alcoholates and organometallic compounds soluble in organic solvents, followed by solvent removal and hydrolysis. The resultant composite can be applied to a metal substrate or other substrate and once sintered or annealed at the appropriate temperature results in an improved quality, high strength ceramic coating.		

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PROCESS FOR PREPARATION OF HIGH TEMPERATURE  
COMPOSITE CERAMIC MATERIALS AND COATINGS

RELATED APPLICATION

This application is a continuation-in-part of application Serial No. 08/163,652, filed December 6, 1993.

BACKGROUND OF THE INVENTION

5        This invention pertains to ceramics and, more particularly, to a process for preparing and using metal alcoholates to produce high strength composite ceramic materials and coatings.

10        Over the years, various conventional industrial methods to produce composite ceramic materials and coatings have been suggested, such as: (1) solid state high temperature treatment of blends of oxides; (2) gas-phase decomposition of volatile organometallic compounds; (3) controlled co-hydrolysis of metal alkoxides or carboxylates  
15        with co-deposition of the resulting composites, followed by sintering (sometimes referred to as the "sol-gel" technology); and (4) plasma deposition of oxides.

20        Various electrochemical techniques have also been used. One conventional technique for producing tantalum, germanium, silicon, titanium, and zirconium ethylates is by electrochemical cathodic solution of a particular metal in electrolytes involving  $\text{NH}_4\text{Cl}$  or  $(\text{CH}_3)_4\text{NCl}$ . Electrolysis is carried out with 2 amps of direct current in a boiling electrolyte under a voltage of 40-60 volts using a carbon  
25        cathode. This method, however, can be applied for only a limited number of metals and attains a relatively low yield of 70-78%.

30        Another electrochemical technique is the preparation of materials by anode dissolution. Silicon ethylates have been prepared by electrochemical anode solution of an iron-silicide anode in an alcohol solution of  $\text{Fe}_2(\text{SO}_4)_3$  or  $\text{ZnCl}_2$  using a carbon cathode. Electrolysis is carried out at a voltage of 70 volts and 2 amps current. Such conditions, however, only attain a relatively low yield of 60%.

35        Electrochemical techniques have further been used to produce ethylates of iron, cobalt and nickel by electrochemical anode solution of a particular metal in an

alcohol electrolyte solution with lithium perchlorate and lithium bromide. Such prior art electrolysis has been carried out at 50-60 volts at a current of 1.5 amps using a carbon cathode, but only attains a yield of 75%. This prior art process is also limited by the small amount of metals.

Another electrochemical technique includes synthesis by use of a cell with non-separated anode and cathode space, a stirrer and two electrodes including a carbon cathode and a metal anode. This prior art electrochemical technique produces metal alcoholates with atomic numbers 14-82 by particular metal electrochemical anode solution using direct current in an electrolyte with  $C_1-C_4$  alcohol and conductive ingredient of  $R_4NX$  formula, where R- is hydrogen or alkyl, N is nitrogen, and X is a halogen. Electrochemical solution of the anode takes place at a current of 0.5 to 2 amps and a voltage of 40-60 volts. The electroconductive ingredient is  $NH_4Cl$  and  $(CH_3)_4NCl$ . Electrosynthesis is held in the boiling electrolyte. Yield of products is 68-78%. The disadvantage of this prior art method is that it can't be used to produce a number of metal alcoholates and the synthesis apparatus is complex. Furthermore, the yield is only 68-78%.

The above electrochemical methods suffer from high energy expenses and require sophisticated and expensive equipment. Furthermore, the above electrochemical methods and conventional industrial methods to produce composite ceramic materials and coatings are often difficult to use, cumbersome, inefficient, costly, and frequently result in non-uniform products and low yields. As a result, the quality, strength, and temperature resistance of the composite ceramics is rather poor.

It is, therefore, desirable to develop an improved process which overcomes most, if not all, of the preceding problems.

SUMMARY OF THE INVENTION

An efficient alkoxy process is provided to prepare high-temperature, high-strength, composite ceramics. Advantageously, the process is economical, reliable and effective. Desirably, the novel process achieves high yields of homogenous uniform composite ceramics.

The inventive technology has produced unexpected surprising results. Tests show that turbojet alloys protected with ceramic composite coatings created by means of the new technology withstand long time exposure in the presence of oxygen at 2000° C without perceptible corrosion. In the cases of steel tubes, alumina ceramic coating created with the use of the new technology provides long time protection in the air at the temperature up to 1100° C. Good protection for pistons in diesel engine has also been achieved with alumina-silica ceramics created by means of the new technology.

To this end, the inventive alkoxy process includes electrochemical preparation of metal alcoholates and organometallic compounds which are soluble in organic solvents, by electrolysis of a metal material in an alcohol in the presence of an electroconductive additive. The electrolysis can be carried out by electrode dissolution by alternating current (AC), direct current (DC), or combinations thereof. The metal material can be elemental metal, a metal compound, a metal alkoxide, or an organometallic precursor. The alcohol is preferably ethanol, propanol, butanol, pentanol, or hexanol, and may be of primary, secondary, or tertiary structure, and chosen to ensure the correct range of volatility and reactivity in subsequent processing. It may be desirable to use other alcohols, alkoxy-alcohols or amino-alcohols containing the  $\text{NR}_2$  group for particular metals. The organic solvent can be: an enamel solvent, gasoline, petroleum ether, naphtha, benzene, toluene, acetone, hexane, or ethylcellosolve. In some circumstances it may be desirable to use other organic solvents.

Other electrolytes can also be used to enhance electrolysis, such as: acetonitrile, dimethyl-sulfoxide, dimethyl-formamide, benzene, and toluene.

The metal alcoholates can comprise alcoholates of one  
5 or more of the following metals: magnesium (Mg), aluminum (Al), gallium (Ga), indium (In), yttrium (Y), lanthanum (La), cerium (Ce), titanium (Ti), zirconium (Zr), hafnium (Hf), neodymium (Nd), tantalum (Ta), iron (Fe), cobalt (Co), nickel (Ni), calcium (Ca), selenium (Se),  
10 praseodymium (Pr), samarium (Sm), silicon (Si), tellurium (Te), ytterbium (Yb), tin (Sn), scandium (Sc), lead (pb), vanadium (V), terbium (Tb), niobium (Nb), and gadolinium (Gd).

In the novel process, homogeneous monomolecular layers  
15 or regions of metal alcoholates and organometallic compounds are deposited on a substrate to produce the desired composite ceramics. Specifically, the electrochemically prepared metal alcoholates and organometallic compounds soluble in the organic solvents  
20 are applied and coated on the substrate, using a very dilute solution to insure formation of a uniform, homogenous monolayer of high surface activity. After the hydrolysis, the coated substrate is heated, preferably sintered, and the organic solvents are evaporated  
25 (vaporized).

The substrate can comprise: metal, catalyst, ball bearings, a turbojet, combustion engine, chemical equipment, pipelines, aerospace components, pistons, cylinders, automobile parts, high temperature apparatus,  
30 tools, dental coatings and teeth, optical lenses, semiconductors, and superconductive materials. The ceramic material provides a superior coating and excellent insulation, as well as superb petrochemical catalysts and oxidized ceramics for electronics.

35 The solvent evaporation and hydrolysis are enhanced by moist air or humid air, or by an inert gas saturated with or containing water vapor. As used in this application

"moist air" is ambient air containing humidity at room temperature. Humidity is controlled by adding water vapor (steam) or by drying the air. Temperature and humidity control effect the desired rate of hydrolysis and solvent removal. Moist air comprises oxygen, nitrogen and water vapor (moisture). Air can also contain trace amounts of elements and compounds, such as argon, carbon dioxide, neon, helium, methane, krypton, nitrous oxide, hydrogen, etc. The alcoholates are hydrolyzed to oxides.

The process of the present invention provides high purity uniform ceramic composite coatings on metals and other substrates, such as optical glass or other inorganic materials. Desirably, the inventive process achieves: (a) exactly prescribed stoichiometry of the components in bulk coating; (b) good homogeneous ceramics; (c) high adhesion strength to the substrate surface; (d) substantial decrease of energy expenses; (e) faster sintering procedures; (f) lower sintering temperature; and (g) high quality ceramic film.

The inventive technology provides a process for preparation of high temperature composite ceramic materials and coatings. The special process comprises an electrochemical step for preparation of starting alcoholates, preparation of raw composites, and application of coatings. A direct one-step electrochemical method for preparation of high-purity metal alcoholates and organometallic compounds soluble in organic solvents is attained by electrode dissolution of metals in the corresponding alcohol. This step is then followed by removal of the solvent from the metal alcoholate and organometallic compounds and subsequent hydrolysis. The coatings can be produced from the raw composites by heating to about 400° C for an hour. In some circumstances, it may be desirable to heat at different temperatures and/or for different periods of time.

A more detailed explanation of the invention is provided in the following description and claims.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The development of new types of construction and functional ceramics is one of the most important fields of modern material science. The application range of ceramic materials covers turbojet and combustion engines, electronics, superconductive materials, teeth prosthesis, protective coatings, insulation, ball bearings, optical lenses, etc. The invention is particularly useful for electrochemical synthesis of metal alkoxides and formation of ultra-thin coatings of ceramics.

The inventive alkoxy technology for the preparation of composite ceramic materials includes a universal electrochemical method for preparation of starting alcoholates comprising a direct one-step electrochemical method for preparation of high-purity metal alcoholates and organometallic compounds soluble in organic solvents. The alkoxy method comprises electrode dissolution of metals in the corresponding alcohol in the presence of an electroconductive additive using either a direct or an alternating current. The method is ecologically pure and free of toxic waste. The main by-product is gaseous hydrogen which can be safely emitted into the atmosphere or used as a fuel. In case of combustion use, pure water is the only product. Desirably, no electrolyte is consumed during the electrolysis. Advantageously, electrochemical preparation avoids the impurities inevitably present when salt exchange is used for electrolysis since corrosion of metals by salt impurities is a real problem.

The inventive alkoxy technology for the preparation of composite ceramic materials also includes preparation of raw composites. To achieve fine homogeneous composite ceramics and an exact stoichiometry of the components throughout the bulk, a new approach to the preparation of raw composites has been developed in accordance with this invention. This is achieved by using metal alcoholates and organometallic compounds soluble in mixtures of organic solvents. The processes of solvent removal and subsequent



hydrolysis have been elaborated so as to allow preparation of raw composites highly homogeneous in composition.

The inventive alkoxy technology for the preparation of composite ceramic materials further includes production and application of coatings and their subsequent sintering. The technology ensures good adhesion of the coatings to metals and a high protection against high-temperature oxidation. The good adhesive strength of the ceramic/metal joints results from extremely fine and homogeneous distribution of alkoxides in the raw composite. The alkoxides provide high surface activity, which promotes strong adsorption of monolayers which are sequentially added and stabilized by reaction. The high chemical homogenous characteristics of the raw composite also enhances the quality of the coating, increases its working temperature and reduces the energy expenses on sintering. Preferably, the substrate surface is cleaned and treated, e.g. degreased, etched, etc., before surfacing or application of the composite ceramic.

The process of ceramic coating includes the steps of: (1) cleaning the substrate surface and fat removal; (2) preparing the alkoxide solution (dry air and dry solvents); (3) substrate coating, up to 10 layers, with the intermediate effect of water vapor under the temperature of 70° C after each coating (in some cases room air is sufficient); and (4) annealing in an inert (in some cases) atmosphere. The temperature scale depends on the substrate.

Uniform fine-grain ceramics of great integrity can be made using alkoxides. Bonding, hydrolysis and volatility are important in selecting the alkoxides to be used. Control of reaction rates can also be important.

Very fine powders can be converted into ceramics to create successive monolayers on surfaces. Equal rates of metal hydroxide formation and evaporation of alcohol are achieved. This allows the deposition of a highly uniform monolayer. These thin layers will be translucent.

Equipment helpful for carrying out the process of the invention are: (a) a standard electrolyzer with (b) an anode made of Zr, Al, Hf, Ti, etc. and (c) a cathode made of Pt, Ni, etc., (d) a rotor evaporizer, and (e) a vacuum oven, preferably a high-temperature vacuum oven, for annealing or sintering, from 20 until 1500° C to 1700° C.

In one test, the alkoxy technology of the invention was used to produce a protective coating of zirconium oxide (a solid solution of 10% yttrium oxide in zirconium oxide). The thickness of the coating was 45 mcm. The adhesion strength of the coating to thermostable alloys ranged from 125 to 175 kg/cm<sup>2</sup>. The Knorr hardness of the coating was 720-950 kg/mm<sup>2</sup>. The density of the coating was 4.5-5.7 g/cm<sup>3</sup>. The complete conversion of the raw composite into a homogeneous cubic phase was achieved by heating to 400° C for one hour. The coating withstood six 10 minute thermocycles 30° C to 2000° C to 30° C, and a 1.5 hours exposure in air at 2000° C without perceptible corrosion. In further tests, sintering of yttrium and zirconium oxides and zirconium oxides, a similar phase transition occurred at 1100° C and took 6 to 8 hours.

Advantageously, the alkoxy method of the invention can be readily realized on an industrial scale as a continuous process. A pilot plant for continuous production of tetrabutyltitanium from titanium powder has been developed. The inventive method has also been used for preparation of yttrium (Y), zirconium (Zr), and hafnium (Hf) isopropylates. The current efficiency for the inventive processes comes to 85-92% with yields to 96-98%.

The inventive alkoxy method has unexpectedly and surprisingly been found to be successful in preparation of the alcoholates of Mg, Al, Ga, In, Y, La, Ti, Zr, Hf, Nb, Ta, Fe, Co, Ni, Ca, Se, Pr, Ce, Sm, Si, Te, Yb, Sn, Pb, V, Nd, Gd and Tb. Advantageously, all of the various alcoholates can be prepared using exactly the same equipment and technological techniques. This represents a

substantial savings in equipment and energy resources.

The above described alkoxy-technology can provide high-temperature ceramic materials and coatings with various compositions and a wide spectrum of desirable properties. Cylinders for a diesel engine were treated in accordance with this invention. Tests were conducted to compare the treated cylinders with untreated cylinders. The composite ceramically coated cylinders performed better showing no evidence of erosion after six months of operation.

Some of the many advantages of the electrochemical method and ceramic preparation process of the invention are: (a) technological simplicity; (b) ecological attractive; (c) no toxic by-products are formed; (d) safe; (e) the process is cyclic and allows complete regeneration of the electroconductive additive and solvent; (f) the process can be readily made continuous; and (g) standard electrolyzers and equipment can be used in the process.

Preferably, all steps in creation of ceramic coating film should be carried out on the surface of the covered solid substrate. Any type of movement of any component of the composite should be excluded.

In the process, soluble organometallic precursors are produced and used which can be easily transformed into ceramic under mild reaction conditions. Also, organometallic compounds are selected and used which are quite stable in organic solvents and can be easily placed on substrate surface without any decomposition. The organic solvents should be volatile enough to be easily removed from the substrate surface.

The reasons for utilizing soluble metal organic precursors is to achieve the objective of precise control of stoichiometry over the entire exposed area of the object being coated. Provided a suitable solvent is chosen any metal alkoxide will work. Several are listed below and others will work as well. Given freedom of choice of solvent, any stable alkoxide is suitable. The universe of

compounds is  $M(OR)_n$  where the subscript  $n$  is chosen to satisfy the valence of the central metal moiety. It is desirable to use metal organic compounds which are stable in organic solvents to achieve precise control of reaction stoichiometry over the surface of the object.

The universe of compounds is metal alkoxides of the general formula  $M(OR)_n$  wherein:

M is a metal comprising Mg, Ca, Se, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Yb, Al, Ga, In, Ti, Zr, Hf, Si, Sn, Pb, V, Nb, Ta, Fe, Te, Co, Ni, or Sc;

O is oxygen;

R is a radical comprising  $C_1$ - $C_6$  primary, secondary and tertiary alkyl groups, or alkoxo-alcohols containing the OR group, or amino-alcohols containing the  $NR_2$  group;

$n$  is an integer (whole number).

The organic solvents should be volatile enough to be easily removed; e.g., by evaporation at low or moderate temperatures. The objective is to concentrate uniformly the concentration of metal alkoxides on the surface of the object without disturbing the homogeneity of the solution. The final objective of this step is to deposit a uniform residue of mixed or pure metal alkoxides on the surface of the substrate in a layer free of voids or inclusions. Examples of solvents which may be utilized are isopropyl alcohol (isopropanol), hexane, ethylcellosolve, enamel solvent, gasoline, petroleum ether, benzene, toluene, naphtha, acetone. The alkoxide concentration in the solvent can be 5% to 10%.

It is desirable to use volatile solvents. While using one or another solvent, one should take into account not only time necessary for the treatment of the metal piece (substrate) but the porosity of the substrate or support. The more porous substrate there is, the more volatile solvent can be used. The solvent and the rate of evaporation of solvent can be determined based upon the complexity of the part being coated. If the time of solvent evaporation from a metal surface is increased,

dispersion is also increased and the coating becomes harder and of higher quality. Control of the rate of the solvent removal should be exercised.

Preferably, chemical transformation of organometallic compounds start only after the fixation of the precursor on the substrate surface. Chemical transformation of the precursor should not be too fast. Fixation refers to the adsorption, e.g. chemisorption, of metal alkoxides on clean metal surfaces. Fixation is the adsorption process in which alkoxides are kept on the surface after removal of a solvent. Since homogeneous solutions of alkoxides in concentration of not more than  $1 \cdot 10^{-1}$  M are used, a monomolecular film layer having phenomenal surface activity is obtained. This property helps in further successful growth of layers one after another. This results in an intermediate step of a uniform layer before the final preparation of the surface film prior to changing the chemical composition of the adsorbed molecular film.

The best reagent for metal alkoxide hydrolysis was found to be moist air at a moderate temperature of 20° C to 70° C at atmospheric pressure. Nearly equal rates of metal hydroxides formation and evaporation of produced alcohol are attained. The proximity of these rates avoids the distortion of geometrical arrangement of precursor atoms. The rate of reaction is controlled to ensure a uniform surface coating is achieved.

Hydrolysis is an important first step reaction. It is the control of the hydrolysis step which can be central to controlling the decomposition of the alkoxide to the oxide and alcohol. This hydrolysis is conveniently controlled by using the moisture in ordinary room air, "moist air". In some circumstances, it may be desirable to use other mild hydrolyzing agents for the chemical conversion step.

The main reason organometallic precursors are used is that crushing, even almost perfect crushing, of oxides and their mixtures gives after subsequent annealing undesirable bad coatings and products with a large amount of slivers.

Coatings, obtained according to the process of the invention have great surface activity. Homogeneous monomolecular layers of coatings are obtained.

5 In the case of zirconium oxide stabilized by  $Y_2O_3$ , this leads to an uniform distribution of alloy additives; that is, to the conservation of the stoichiometric ratio and to an increase of particle dispersion.

10 Ceramics obtained after annealing or sintering having excellent characteristics. X-ray diffraction data for the intense absorption bands of ceramic  $ZrO_2$  containing  $Y_2O_3$  (6-10 mol % at a caking temperature of 800° C to 1200° C degrees are shown in the following Table:

Table: X-Ray Diffraction

d (Å)
2.971
2.578
1.810
1.555
1.498

20

25 Heating preferably comprises heating followed by annealing or sintering at mild conditions. It is preferred to heat at 400° C degrees during the synthesis of some ceramics. For example, a temperature of 400° C is a desirable condition for the mixture with crystal water, for example  $ZrO_2/Y_2O_3$ , formed on a metal surface, to transform from the amorphous to the crystal state, namely to the cubic modification of  $ZrO_2$  alloyed with  $Y_2O_3$  (6-10%). But in order to obtain a firmly attached ceramic coating on the surface, the product should be annealed at the temperature 30 from 850° C until 1200° C to 1500° C degrees for 1 hour. Annealing conditions can be varied taking into account alloy properties (refractory alloys or stainless steel).

In the case of  $\text{Al}_2\text{O}_3$  (the initial compound  $\text{Al}(\text{OC}_3\text{H}_7)_3$ ), an annealing temperature of  $450^\circ\text{C}$ - $500^\circ\text{C}$  is sufficient for duraluminium. An annealing temperature of  $850^\circ\text{C}$  is sufficient for stainless steel.

5        It may be helpful at this stage to define the term "metal alkoxide". The binary metal alkoxides have the general formula  $\text{M}(\text{OR})_x$ . Metal alkoxides involve M-O-C bonds which are polarized due to the highly electronegative character of oxygen. The degree of polarization in an  
10        alkoxide molecule depends upon the electronegativity of the central element (M) and the nature of these compounds varies from essentially covalent volatile monomers as in cases of electronegative elements like silicon, germanium, phosphorus and sulphur to more electrovalent polymeric  
15        solids in the cases of electropositive elements such as the alkali and alkaline earth metals as well as the lanthanons. For derivatives of the same element, the covalent character of the M-O bond increases with greater inductive effect of the alkyl group. For example, amongst the isomeric  
20        butoxides of an element, the tertiary butoxide should have the highest covalent character. The decreasing order of molar conductivities of sodium methoxide, ethoxide, isopropoxide and tert-butoxide in their parent alcohol (i.e., 92.0, 45.0, 2.5 and 0.01 mhos respectively) appears to  
25        arise at least in part from the increasing +1 inductive effect of the alkyl group. The polarity of the M-O bond may also be partially offset in cases of electrophilic metals which undergo covalency expansion by intermolecular coordination through the oxygen atoms of the alkoxy groups.  
30        This type of molecular association appears to be sensitive to factors such as the ramification of the alkyl group.

      The method required for the synthesis of alkoxy derivatives of an element generally depends on its electronegativity. Highly electropositive elements with  
35        valencies up to three ions (like alkali metals, alkaline earth metals and lanthanons), react directly with alcohols

with the liberation of hydrogen and formation of metal alkoxides. In the case of comparatively less active metals, like beryllium and aluminum, a catalyst may be required for successful synthesis of alkoxides. Another  
5 general method of synthesis applicable to electronegative elements (like boron, silicon, and phosphorus) is the reaction of their covalent halides with the appropriate alcohol. This method employing the anhydrous chloride as  
10 starting material does not appear to effect complete replacement of halide when the central metal atom is comparatively less electronegative. However, in many cases (e.g. Fe, Ti, Th, Nb, lanthanons, etc. excluding the strongly electropositive metals like sodium, calcium etc.), the replacement of halide could be forced to completion by  
15 the use of bases such as pyridine, ammonia, etc.

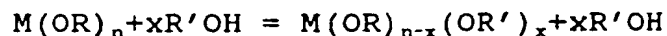
In view of the very slight acid character of alcohols (even weaker than that of water), reaction of metals with alcohols is best performed with strongly electropositive elements, such as alkali metals and alkaline earth metals.  
20 In the case of the alkaline earths and even more so for the less electropositive elements such as magnesium, beryllium and aluminum, a catalyst (iodine, mercuric chloride, mercuric iodide etc.) may be helpful. A similar role appears to be played by oxygen in the reactions of thallium  
25 with alcohol; thallus oxide or hydroxide formed on the surface of the metal appears to react with alcohol whereas the metal surface appears to be inert.

The elements of group II of the periodic table, for example beryllium and magnesium may not react directly with  
30 alcohols, but may require a catalyst. For example, beryllium metal reacts with ethanol in the presence of a catalyst (e.g. iodide, mercuric chloride or beryllium dichloride) to form beryllium diethoxide.

Metal halides have been used quite extensively as  
35 starting materials for the synthesis of a large number of metal alkoxides. Metal chlorides can be dissolved in alcohol.



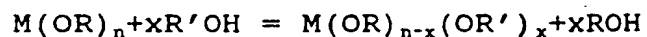
Alkoxy derivatives of the elements tend to react with all hydroxy compounds resulting in the replacement of their alkoxy groups. For example, the reactions of alkoxides with alcohols, generally termed as alcoholyses or alcohol interchange reactions, can be represented by the following general equation:



These alcoholysis reactions can be used to synthesize alkoxy derivatives of various elements like zinc, beryllium, boron, aluminum, gallium, indium, carbon, silicon, germanium, tin, titanium, zirconium, hafnium, cerium, thorium, vanadium, iron, antimony, niobium, tantalum, selenium, tellurium, uranium, neodymium, erbium, yttrium, and ytterbium.

In order to complete an alcoholysis reaction, an excess of the higher boiling reactant alcohol would be required. This can sometimes be avoided by use of a solvent which is higher boiling than even the reactant as well as the alcohols. When the original alkoxide is ethoxide or isopropoxide, the use of an organic solvent like benzene offers an added advantage by virtue of the formation of a minimum azeotrope with ethanol or isopropanol which facilitates the removal of the alcohol.

Metal alkoxides react with a variety of primary secondary and tertiary alcohols as well as phenols to set up the following type of equilibrium:



In some cases, a solvent like benzene which forms an azeotrope with the liberated alcohol (e.g., ethanol and isopropanol) facilitates fractionation of the liberated alcohol, but also makes it possible to carry out the reaction in any stoichiometric ratio of the reactants to get the desired mixed alkoxides. In some cases (e.g. methoxides) the forward reaction is greatly facilitated by the instantaneous separation of the insoluble methoxide on mixing the alkoxide with excess of methanol. The above alcoholysis reactions can be widely applied for the

synthesis of a large number of metal alkoxides.

The physical properties of metal alkoxides are as follows. The alkoxy derivatives of metals have at least one M-O-C system. Due to the strongly electronegative character of oxygen, alkoxides of metallic elements exhibit a strongly polar character. Metal-oxygen bonds in these derivatives may have around 65% ionic character for metals with electronegativity values of 1.5-1.3 (e.g. aluminum, titanium and zirconium) to about 80% ionic character for more electropositive metals with electronegativity values of the order of 1.2-0.9 (e.g., alkali metals, alkaline earths and lanthanons). However, most of these alkoxides show a fair degree of volatility and solubility in common organic solvents; properties which can be considered as characteristic of covalent compounds.

For a homologous series of monomeric alkoxides  $M(OR)_x$ , the volatility decreases with increase in n-alkyl chain length while in an isometric series of monomeric alkoxides branching of the alkyl chain may lead to a small increase in volatility due to the effect of the shape of the molecule on its intermolecular forces. In the case of oligomeric alkoxides  $[M(OR)_x]_n$  (where  $n = 2, 3, 4$  etc.), the intermolecular forces are profoundly affected by the strength of the metal alkoxide-metal bridges. If these bridges are so strong that the oligomeric molecule volatilities intact, then its volatility will be decreased relative to a monomer due to its greater size and concomitant intermolecular forces. If the bridges are dissociated either partially or completely, the volatility is affected by the energy of dissociation. In either case, the volatility will be sensitive to the shape of the alkyl group which by virtue of steric hindrance to intermolecular coordination may affect the degree of polymerization.

Most of the metal methoxides are comparatively non-volatile and insoluble in common organic solvents. The primary alkoxide derivatives of alkaline earth and other metals of group II are generally insoluble non-volatile

compounds whereas their secondary and tertiary alkoxides tend to be comparatively more volatile and soluble in organic solvents. Alkoxides of Group IV elements such as silicon and germanium alkoxides can be highly volatile.

5 Alkoxide derivatives of sulphur, selenium, tellurium, arsenic and antimony are highly volatile. Alkoxide derivatives of divalent copper, chromium, nickel, cobalt and manganese are all insoluble non-volatile products.

10 Metal alkoxides are generally very reactive species which may be due to the presence of electronegative alkoxy groups making the metal atoms highly prone to nucleophilic attack. These metal alkoxides are, therefore, susceptible to hydrolysis by atmospheric moisture.

15 Metal alkoxides readily react with excess of hydrogen halides or acyl halides giving the metal halides. However, by using stoichiometric amounts of these halides, the metal halide alkoxides may be prepared.

Fundamentally, the uses of metal alkoxides depend on their chemical reactivity coupled with their volatility and solubility in common organic solvents. The chemical reactivity is manifest in the variety of catalytic applications of the alkoxides, ranging from redox catalysts for aluminum alkoxides, olefin polymerization catalysts for titanium and vanadium alkoxides to accelerators for protective coatings. Ultimately the alkoxides are valuable precursors to the metal oxides through hydrolysis. Where high purity is at stake, the metal alkoxides offer considerable advantages as starting materials for the preparation of high purity oxides. This aspect has been stimulated by the rapid developments in the microelectronics field where the advantage of the ease of hydrolysis of the volatile metal alkoxides and the application of ceramics is especially appreciated.

35 Hydrolysis of metal alkoxides causes the formation of hydroxides or hydrated oxides. However, when restricted amounts of water are added, these metal alkoxides undergo partial hydrolysis reactions yielding in some cases

products of definite composition as oxide alkoxides  $MO_n(OR)_x$ . The hydrolysis of titanium normal alkoxides decreases with the increase in chain length.

Alkoxides are extremely useful reagents. They are powerful bases-stronger than hydroxide-and, by varying the alkyl group, their degree of basicity, their steric requirements, and their solubility properties can be varied. As nucleophiles, they can be used to introduce the alkoxy group into molecules.

One method of obtaining metal alcoholates of the general formula  $M(OR)_n$  in which

$M = \text{Ti, Mg, Sc, Al, Y, Ga, Zr, Hf, Nb, Ta, Fe, Co, Ni, La, Ca, Se, Pr, Ce, Sm, Si, Te, Yb, Sn, Pb, In, Nd, V, Gd, Nb;}$

$R = C_1-C_6$  primary, secondary and tertiary alkyl groups, alcoxalcohols containing the OR- group, and amino alcohols containing the  $NR_2$  group;

$n = 2, 3, 4, 5,$

is by means of electrochemical dissolution of a metal electrode or metal alloy electrode in an electrolyte containing alcohol and a conductive additive at the electrolyte boiling temperature. In order to simplify the reaction and to increase the yield, the process can be carried out by means of alternating current using as conductive additive materials of the general formula  $KX$ , where:

$K = \text{alkali metal cation, } NH_4^+, \text{ or } NR_4^+;$

$X = Cl^-, Br^-, I^-, BF_4^-, PF_6^-, ClO_4^-,$

in the quantity of 2-20% by weight. The electrolyte can contain  $CH_3CN$ , DMSO, DMFA or benzene in the quantity of 1-20% by weight.

Another method of obtaining metal alkoxides or metal alcoholates of the general formula  $M(OR)_n$  where

$M = \text{Ti, Mg, Al, Y, Zr, Nd, Ta, Ca, Se, Pr, Ce, Sm, Si, Te, Yb, Sn, Pb, Ga, In, Fe, Co, Ni, La groups, Nb, V Gd, Tb, Hf, Sc;}$

R = C<sub>1</sub>-C<sub>6</sub> primary, secondary and tertiary alkyl groups, alcoxo alcohols containing the OR- group, and amino alcohols containing the NR<sub>2</sub> group;

n = 2,3,4,5

5 is by means of alternating current electrochemical dissolution of the corresponding metal electrodes in an electrolyte containing alcohol and salt of general formula KX, where:

K = alkali metal cations, NH<sub>4</sub><sup>+</sup> or NR<sub>4</sub>;

10 X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup> in the quantity of 2-20 % by weight at the electrolyte boiling temperature. Direct current electrolysis is carried out until the corresponding metal oxides precipitation stops. Both the cathode and anode can be made of the same metal.

15 Another method of obtaining metal alkoxides or metal alcoholates of the general formula M(OR)<sub>n</sub> where

M = Metal, chosen from Ti, Mg, Al, Sc, Y, Ga, Zr, Hf, Nb, Ta, Fe, Co, Ni, La groups, Ca, Se, Pr, Ce, Sm, Si, Te, Yb, Sn, Pb, In, Nd, V, Gd, Tb;

20 R = C<sub>1</sub>-C<sub>6</sub>, alcoxo-alcohols, amino-alcohols;

n = 2, 3, 4, 5.

is by means of electrochemical dissolution of a metal anode or metal alloy anode in an electrolyte containing alcohol and a conductive addition and a material having the general  
25 formula KX where

K = Cation, chosen from alkali metal, ammonium or tetra-ammonium base;

X = Cl, Br, I, BF<sub>4</sub>, PF<sub>6</sub>, ClO<sub>4</sub>;

in the amount of 2-20% weight at the electrolyte boiling  
30 temperature and carrying out the process under regular frequency AC. Current can be 0.15-0.5 amps at a voltage of 130-220 volts. It can be useful to add acetonitrile, dimethyl-sulfoxide, dimethyl-formamide or benzene in amount of 1-20% by weight to enhance the electrolyte. Solvents  
35 such as acetonitrile, dimethyl-formamide, dimethyl-sulfoxide cause an increase in electrical conductivity when

added. Polar solvents have more dielectric constant than some alcohols, especially higher alcohols. Addition of nonpolar solvents, such as benzene or methyl benzene, cause more adsorption of the solvent on the electrode increasing the solubility of slightly soluble alcoholates. Operating the process by this way, one can avoid AC-DC converters and increase metal alcoholates yield.

There can be two stages of DC metal alcoholates synthesis: anode process of alkoxohalides of particular metal synthesis (halogen-ion from electroconductive material) and a cathode process of intermediate products reduction on a cathode with the final product of particular metal alcoholate. Hydrogen relaxation and metal alcoholate formation can take place on a cathode in metal-chlorides cathodic reduction in alcohol solutions. When the process is carried out by AC, intermediate products formation take place in anodic half-period (alkoxohalides of metals). And they will be reduced to appropriate alcoholates in cathodic half-period. Intensive stirring is not needed, as both synthesis stages take place in a cell on electrode surface. Also, solubility of these intermediates are not required. The change in electrode surface potential does not effect local increase of alkoxohalides concentration or alcohol decomposition.

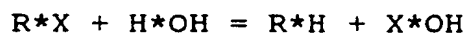
It is preferred that the process of the invention be based on the usage of direct and alternating current of industrial frequency or changeable frequency in connection with the nature of the metal and electrolyte. In the process, electrolysis is carried out in the solution of corresponding alcohol plus neutral organic solvents with the aim to decrease the voltage and thereby decrease the overall energy expenses.

As discussed above, electrolysis is preferably performed in two stages, where the first-stage electrolysis is held under DC up to particular metal oxides precipitant formation and the second stage is held under AC. Running the process by this way, one can use commercial alcohols,

which have up to 4% of water fraction. In the first DC stage water decomposes. Metal alcoholates synthesis takes place in the second AC stage.

5 The anode and cathode can be made of the same or different materials. Treatment of the reaction mixture is preferably carried out without distillation to decrease energy expenses. The electrolytic processes can be carried out in dry or moist air.

10 Hydrolysis is the chemical decomposition or splitting of a compound by means of water, as in the following general equation:



15 Water, in the form of its hydrogen and hydroxyl ions, adds to the cleaved compound. The addition of water is generally catalyzed by ions and without added ions may be a very slow process. Consequently, the addition of acid or base increases the concentration of hydrogen or hydroxyl ions with a corresponding increase in the rate of hydrolysis. Certain enzymes also catalyze the hydrolysis of some organic compounds.

20 Alcoholates of metals are prepared by the inventive process. By almost any classification roughly three-quarters of the elements are metals, including the Periodic Table Groups IA, IIA, all of the B groups, IIIA with the possible exception of boron, IVA with the possible exception of carbon and possibly silicon, VA with the exception of nitrogen and phosphorus, and VIA with the exception of oxygen and sulfur.

30 In general, metals are solids with a metallic luster, conductive of electricity by electron flow, malleable, and of high physical strength. In compound form the metals have positive valences. Probably their most important characteristic is that when used as metals they are predominately in element form or alloyed with other metals.

35 Metal occur most commonly as oxides or sulfides in ores that contain variable amounts of materials like clay, silica, granite, etc., from which the metallic compounds

must be separated. Electrolysis offers the best means, and in some cases the only practical means, of producing many pure metals. Deposition from aqueous solution is used to prepare cadmium, copper, cobalt, gallium, indium, manganese, thallium and zinc. It is valuable in the application of many metals as electrodeposited coatings, among them cadmium, copper, cobalt, chromium, palladium, platinum, rhodium, indium, tin tungsten, nickel and zinc.

The word "metal" has two somewhat different meanings. Chemically, a metal is a chemical element which tends to form positive ions in solution and whose oxides form hydroxides rather than acids with water. Physically, a metal is a phase containing free electrons which give it certain characteristic properties such as high electrical and thermal conductivity, metallic luster, and, often, plastic formability. These phases need not be pure substances; when they are not, they are called alloys.

In metallic phases, the atoms are held together by chemical bonds characterized by mobile or "free" electrons. These are responsible for their electrical conductivity, which is of the order of  $10^{25}$ , while non-metals generally have a conductivity of less than  $10^{-10}$ . The free electrons are also efficient conductors of heat so metals are typically nearly a thousand times as good conductors of heat as non-metals. For nearly all metals and alloys the conductivity of heat is nearly proportional to the conductivity of electricity. This ratio changes with temperature because electrical conductivity is almost inversely proportional to absolute temperature, while thermal conductivity is relatively constant with changing temperature.



Table of Electrochemical Properties of Metals

Metal	Ion	$E_0$
Lithium	$\text{Li}^+$	+2.957
Potassium	$\text{K}^+$	+2.922
Strontium	$\text{Sr}^{++}$	+2.92
Barium	$\text{Ba}^{++}$	+2.90
Calcium	$\text{Ca}^{++}$	+2.87
Sodium	$\text{Na}^+$	+2.712
Magnesium	$\text{Mg}^{++}$	+2.40
Titanium	$\text{Ti}^{++}$	+1.75
Aluminum	$\text{Al}^{+++}$	+1.7
Beryllium	$\text{Be}^{++}$	+1.69
Uranium	$\text{U}^{+++}$	+1.4
Manganese	$\text{Mn}^{++}$	+1.1
Zinc	$\text{Zn}^{++}$	+0.758
Chromium	$\text{Cr}^{++}$	+0.6
Iron	$\text{Fe}^{++}$	+0.44
Cadmium	$\text{Cd}^{++}$	+0.397
Cobalt	$\text{Co}^{++}$	+0.29
Nickel	$\text{Ni}^{++}$	+0.22
Tin	$\text{Sn}^{++}$	+0.13
Lead	$\text{Pb}^{++}$	+0.12
Bismuth	$\text{Bi}^{+++}$	-0.2
Copper	$\text{Cu}^+$	-0.51
Silver	$\text{Ag}^+$	-0.799
Mercury	$\text{Hg}^{++}$	-0.86
Gold	$\text{Au}^+$	-1.5

In the process organometallic compounds are produced. An organometallic compounds is one which contains a metal (M) attached directly to carbon. Organometallic compounds (RM) can be prepared of practically all the metals. Simple organometallic compounds have only R groups attached to the metal, as  $\text{R}_4\text{M}^{\text{IV}}$ . Mixed organometallic compound have

both R and X groups attached to the metal, as  $R_2M^{III}X$ . The simple types may be further divided into symmetrical (as  $C_2H_5HgC_2H_5$ ) and unsymmetrical (as  $C_2H_5HgC_4H_9$ ) classes. Within these general groups there are many types of organometallic compounds. Those having but one metal may contain one or more R groups and one or more X groups, depending on the valence number of metal and the stabilities of the organometallic compounds. Furthermore, two or more of the same or different metals may be present as in  $CH_2(ZnI)_2$ ,  $(C_6H_5)_3SiSn(C_6H_5)_3$ , and  $(C_6H_5)_3GeLi$ .

Organometallic compounds may be classified in various ways, but one convenient system is by groups in the Periodic Table., In any group or subgroup the higher the ionization potential of the metal, the less reactive will be its organometallic compounds. Organometallic compounds may be grouped by relative reactivities on the basis of two reactions: (a) addition to an olefinic linkage; and (b) addition to a carbonyl group. The highly reactive compounds add to both. The relatively unreactive compounds add to neither functional group.

Organometallic compounds derive from interaction of an RX compound with a metal, or its alloy, or amalgam. Generally, organometallic compounds can be made from all metals and metalloids. Reactive and moderately reactive organometallic compounds can undergo reactions with all functional groups. General reactions shown by RM compounds are oxidation, and cleavage by acids. General rules for the reactivities of RM compounds is that the organometallic compounds of the alkali metals form the most reactive group, and in this group the order of increasing reactivity is: Li, Na, K, Rb, Cs.

The physical properties of RM compounds vary over wide ranges. Some (like trimethylboron) are gases; many are liquids: but for the most part (particularly those having aryl groups) they are solids.

As a general rule, the less reactive organometallic compounds are unaffected by water; but the moderately and

highly reactive RM compounds are decomposed vigorously by water. Water or other hydroxylated compounds should not be used as solvents for the reactive RM compounds. Some of the less reactive RM compounds can be dissolved in water if the R group in the RM compound has functional polar groups like -COOH, -OH, and -NH<sub>2</sub> which impart water-solubilizing characteristics to the molecule.

In the process, anode dissolution of metals occurs by electrolysis with AC and/or DC electrolysis in alcohol. Alcohols, from a chemical viewpoint, are those classes of organic compounds where one or more hydroxyl (OH) groups are present in a hydrocarbon molecule with no more than one (OH) group attached to a single carbon atom. Three principal types of nomenclature are used. Common or radical names with the word alcohol, are derived from natural sources, e.g., cetyl alcohol or from the hydrocarbon portion, e.g., ethyl alcohol from ethane. With simpler alcohols the common names are most often used. A common name simply consists of the name of the alkyl group followed by the word alcohol. For example: ethyl alcohol, isopropyl alcohol, isobutyl alcohol, tert-butyl alcohol. Substituted carbinol wherein this represents derivatives of methanol. I.U.C. or Geneva name designates the name of the alcohol from the hydrocarbon having the longest straight chain and the alcohol function. In this nomenclature, the final hydrocarbon "e" is replaced by "-ol" (or "-diol," "-triol," etc., according to the number of hydroxyl groups). In the IUPAC system, the parent structure with the longest continuous carbon chain that contains the OH groups is selected. The parent structure is known as ethanol, propanol, butanol, etc. depending upon the number of carbon atoms; each name is derived by replacing the terminal -e of the corresponding alkane name by -ol. In the IUPAC system, the position of the -OH group and other groups attached to the parent chain are identified. Examples of these names are as follows: (CH<sub>3</sub>)<sub>3</sub>COH, tert-butyl alcohol, trimethylcarbinol, 2-methyl-2-propanol.

Alcohols are classified as primary, secondary, and tertiary, depending on the number of hydrogen atoms attached to the carbon atom with the hydroxyl group. A primary alcohol contains two or more hydrogens, one hydrogen for a secondary alcohol, and no attached hydrogens for a tertiary alcohol. Typical examples are:

Methyl alcohol	$\text{CH}_3\text{OH}$	primary $\text{CH}_3\text{OH}$
Propyl alcohol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	primary $\text{CH}_2\text{OH}$
Isopropyl alcohol	$(\text{CH}_3)_2$	secondary $\text{CHOH}$
Trimethyl carbinol	$(\text{CH}_3)_3\text{COH}$	tertiary $\text{COH}$

Alcohols are further characterized by the nature of the hydrocarbon portion of the molecule, e.g. (1) simple aliphatic alcohol, such as ethyl alcohol ( $\text{CH}_3\text{CH}_2\text{OH}$ ); (2) unsaturated aliphatic alcohol, such as ethanol ( $\text{CH}_2=\text{CHOH}$ ); (3) substituted aliphatic alcohol, such as etholamine ( $\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$ ); (4) aromatic alcohol, such as benzyl alcohol ( $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ ); (5) alicyclic alcohol, such as cyclohexanol ( $\text{C}_6\text{H}_{11}\text{OH}$ ); and (6) heterocyclic alcohol, such as furfuryl alcohol ( $\text{C}_4\text{H}_7\text{OCH}_2\text{OH}$ ).

Alcohols in general are colorless liquids or solids. Alcohols occur widely in nature as volatile or essential oils, and as esters in volatile or essential oils, and as esters in volatile oils, fats and waxes. Normal primary alcohols from methanol to butanol are fluid liquids, those from  $\text{C}_5$  to  $\text{C}_{11}$  have an oily consistency, and those from  $\text{C}_{12}$  and higher are solids at room temperature. All monohydroxy alcohols are soluble in organic solvents, and those with one to three carbon atoms are soluble in water. In general, water solubility decreases with increasing molecular weight or complexity of the formula. Conversely, boiling points rise with increases in the same factors. Additional hydroxyl groups increase water solubility and decrease solubility in ether and alcohol.

In general, the reactions of alcohols are primarily those of the hydroxyl groups (unless other active groups are present). The hydroxyl group may be replaced by

halogen or amino groups; the alcohol may be dehydrated; the hydrogen of the hydroxyl group can be replaced by a metal.

Methyl alcohol (methanol, wood alcohol, carbinol) is produced by destructive distillation of hard wood, or by  
5 catalytic synthesis from hydrogen and carbon monoxide.

Ethyl alcohol (ethanol, grain alcohol) is obtained by the fermentation of sugar solution and ashes of starch-containing materials, or synthetically from ethylene. Molasses is the most common raw material for the  
10 fermentation process. Most industrial ethanol is produced in petrochemical plants from the processing of ethane and ethylene.

Isopropyl alcohol (isopropanol) is made by hydration of a propylene-sulfuric acid mixture, although smaller  
15 amounts are a by-product of fermentations.

Normal propyl alcohol comes from the Fischer-Tropsch process and is also a co-product of air oxidation of propane and butane mixtures.

Butyl alcohol (n-butanol) is produced by fermentation  
20 of starches and carbohydrates and also synthetically from ethanol or acetylene. Isobutyl alcohol is mostly synthesized from carbon monoxide and hydrogen at high pressure. Tertiary butyl alcohol is produced from the hydration of 1-butane.

25 Alcohols are compounds of the general formula ROH, where R is any alkyl or substituted alkyl group. The group may be open-chain or cyclic; it may contain a double bond, a halogen atom, an aromatic ring, or additional hydroxyl groups. As the functional group of alcohols, the hydroxyl  
30 group-OH determines the properties characteristic of the family. Variations in the structure of the R group bring about variations in these properties. One reaction, oxidation, which directly involves the hydrogen atoms attached to the carbon bearing the -OH group, takes an  
35 entirely different course for each class of alcohols.

Structurally, an alcohol is a composite of an alkane and water. It contains a lipophilic, alkane-like group and

a hydrophilic, water-like hydroxyl group. Of these two structural units, it is the -OH group which gives the alcohol its characteristic physical properties and the alkyl group which, depending upon its size and shape, modifies these properties. The -OH group is highly polar and is capable of hydrogen bonding: hydrogen bonding to its fellow alcohol molecules to other neutral molecules and to anions. The physical properties of alcohols are shown in the table below.

10

Table: ALCOHOLS

15

20

Name	Formula	Melt	Boiling	Density	Soluble
Methyl	CH <sub>3</sub> OH	-97	64.5	0.793	infinite
Ethyl	CH <sub>3</sub> CH <sub>2</sub> OH	-115	78.3	.789	infinite
n-Propyl	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> O	-126	97	.804	infinite
n-Butyl	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> C	-90	118	.810	7.9
n-Pentyl	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> C	-78.5	138	.817	2.3
n-Hexyl	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> C	-52	156.5	.819	0.6
n-Heptyl	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> C	-34	176	.822	.2
n-Octyl	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> C	-15	195	.825	.05
n-Decyl	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> C	6	228	.829	
Isopropyl	CH <sub>3</sub> CHOHCH	-86	82.5	.789	infinite
Isobutyl	(CH <sub>3</sub> ) <sub>2</sub> CHC	-108	108	.802	10.0
Sec	CH <sub>3</sub> CH <sub>2</sub> CHO	-114	99.5	.806	12.5
tert	(CH <sub>3</sub> ) <sub>3</sub> COH	25.5	83	.789	

25

The acidity of alcohols is shown by their reaction with active metals to liberate hydrogen gas and form alkoxides. Since an alcohol is a weaker acid than water,

an alkoxide is prepared by reaction of the alcohol with the active metal itself. Alkoxides are extremely useful reagents. They are powerful bases-stronger than hydroxide-and, by varying the alkyl group, their degree of basicity, their steric requirements, and their solubility properties can be varied. As nucleophiles, they can be used to introduce the alkoxy group into molecules.

The usage of an anion-exchange membrane is not desirable in the electrochemical process because it causes significant decrease of current density and consequently to increase of the electrolysis time and decrease of efficiency. Membranes also limits the working temperature of the process. Preferably, the temperature should not be higher than 45° C. However the electrochemical process for many metals can be at least as high as 80° C.

Desirably, no pump or magnetic stirrer is needed for circulation of electrolyte. The circulation of electrolyte is provided with boiling electrolyte and/or with bubbles of hydrogen from the cathode. It becomes possible at much higher current density which can not be achieved with membranes.

Rapid thermal annealing (RTA) is not preferred for preparation of high-temperature composite ceramic materials and coatings, because ceramic materials and coating need more time for sintering. Reorganization of atoms in hard phase into corresponding geometrical structure needs adequate sintering time.

In the preferred process, instead of cracking, it is preferred to use hydrolysis at mild conditions, e.g. room temperature or 40° C. These conditions help control the process and organize the needed structure of the composite.

In the preferred process, the hydrolysis procedure is carried out only after the replacement of metal alkoxide on the metal surface of the substrate. This is very important because such a procedure leads to the exact bulk stoichiometry of ceramics and to high adhesion strength.

Two of the many important aspects of the subject

invention are: (1) the universal chemical method for obtaining of metal alcoholates; and (2) the process for preparation of high temperature composite ceramics on the basis of alcoholates.

5           The inventive procedure can be used to produce a polylayer coating in which every layer of the coating possesses the same chemical structure or a different chemical structure, when it is desired to do so. This is especially important for electronic and superconductive  
10           materials.

          Among the many advantages of the alkoxy-technology and ceramic preparation procedures of the invention are:

          1. The electrochemical method used in preparation of the starting compounds for composite ceramics (i.e. metal  
15           alcoholates) is ecologically safe.

          2. A broad range of metal alcoholates can be prepared using the same equipment.

          3. The energy expenses are greatly reduced due to a considerable reduction in temperature and duration of  
20           sintering.

          4. There is a significant improvement in the quality of coatings and an increase in the allowable working temperature due to an exact stoichiometric distribution of the components throughout the bulk of the coating.

25           5. There is a significant improvement in the quality of ceramic materials and coatings due to using alkoxy-technology.

          6. Precursors-metal alkoxides can be easily produced in industrial scale and can be used for ceramic material  
30           and coatings as well as for other purposes.

          7. Outstanding product performance at high and low temperatures.

          8. Superior quality.

          9. Beneficial to the environment.

35           10. Easy to use.

          11. Superb ceramic materials and coatings.

          12. Excellent high strength ceramics.



13. Technological simplicity.
14. Attractive.
15. Economical.
16. Reliable.
- 5 17. Efficient.
18. Effective.

High quality composites produced with the subject alkoxy technology can be advantageously used in: (a) turbojet and combustion engines; (b) high-temperature equipment and engineering; (c) chemical equipment and pipelines; (d) electronics and superconductive materials; and (e) catalysts for various chemical processes. High quality composites produced with the subject alkoxy technology also has many other uses.

15 Impervious ceramic coatings made in accordance with this invention provide corrosion protection and hardness to any metal. For aluminum, the oxide coating which is formed in air oxidation or by electrochemical means can be improved by the addition of alumina of the appropriate crystal phase. The prevention of corrosion or oxidation of all forms of structural metal is another important commercial application of the subject invention.

25 Although embodiments of the invention have been shown and described, it is to be understood that various modifications and substitutions, as well as rearrangements of parts, components, and process steps, can be made by those skilled in the art without departing from the novel spirit and scope of this invention.

CLAIMS

What is claimed is:

5

1. A process for preparing composite ceramics, comprising the steps of:

10 electrochemical preparation of metal alcoholates and organometallic compounds soluble in organic solvents by electrode dissolution of a metal material in an alcohol in the presence of an electroconductive additive;

forming a substantially homogeneous monomolecular layer of metal alcoholates and organometallic compounds on a substrate by

15 applying said electrochemical prepared metal alcoholate and organometallic compounds soluble in said organic solvents to said substrate,

hydrolyzing said alcoholates to oxides and alcohols,

20 heating and evaporating said organic solvents, and

annealing or sintering said oxides, to produce composite ceramics.

25 2. A process in accordance with claim 1 wherein said metal alcoholates comprise alcoholates of a metal selected from the group consisting of: Mg, Al, Ga, In, Yb, La, Ce, Ti, Zr, Hf, Nd, Ta, Fe, Co, Ni, Ca, Y, Se, Pr, Sm, Si, Te, Tb, Sn, Pb, V, Nb, Gd, and Sc.

30

3. A process in accordance with claim 1 wherein said electrode dissolution is by alternating current.

35 4. A process in accordance with claim 1 wherein said electrode dissolution is by direct current.

5. A process in accordance with claim 1 wherein said alcohol comprises an alcohol selected from the group consisting of ethanol, propanol, butanol, pentanol, hexanol, and normal, secondary and tertiary compounds thereof.

6. A process in accordance with claim 1 wherein said applying comprises coating.

7. A process in accordance with claim 1 including heating said metal alcoholates and organometallic compounds.

8. A process in accordance with claim 1 wherein said substrate is selected from the group consisting of metal, an optical lens, a catalyst, a superconductive material, and a semiconductor.

9. A process in accordance with claim 1 including hydrolysis of a metal alkoxide and wherein said electrolyte hydrolyzing agent comprises moist air.

10. A process in accordance with claim 1 wherein said ceramics comprise insulation.

11. A process in accordance with claim 1 wherein said organic solvents comprise at least one solvent selected from the group consisting of: an enamel solvent, gasoline, petroleum ether, naphtha, benzene, toluene, acetone, hexane ethylcellosolv, and isopropanol.

12. A process in accordance with claim 1 wherein said metal alcoholates have the general formula  $M(OR)_n$  wherein M is a metal selected from the group consisting of Mg, Al, Ga, In, La, Ce, Y, Ti, Zr, Hf, Nb, Ta, Fe, Co, Sc, Ni, Ca, Se, Pr, Sm, Si, Te, Yb, Sn, Pb, V, Nd, Gd, and Tb,

R is an alkyl comprising at least one primary alkyl selected from the group consisting of a C<sub>1</sub>-C<sub>6</sub> primary alkyl group, secondary alkyl group, tertiary alkyl group, an alcoxo alcohol containing the OR group, and an amine-alcohol containing the NR<sub>2</sub> group.

n is whole integer ranging from 2 to 5,  
said electrode comprises metal or a metal alloy,  
and

said electrolyte comprises a material having the  
formula KX, wherein

K is a cation selected from the group consisting of an alkali metal, ammonium compound, NH<sub>4</sub><sup>+</sup>, and NR<sub>4</sub><sup>+</sup>, and

X is selected from the group consisting of Cl, Br, I, BF<sub>4</sub>, PF<sub>6</sub>, and ClO<sub>4</sub>.

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13. A process in accordance with claim 12 wherein said electrolyte further comprises a material selected from the group consisting of: acetonitrile, dimethyl-sulfoxide, dimethyl-formamide, benzene, and toluene.

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14. A process in accordance with claim 1 wherein said metal material is selected from the group consisting of: a metal alkoxide, an organometallic precursor, a metal alloy, and a metal compound, and elemental metal.

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15 A process for preparing composite ceramics, comprising the steps of:

electrochemically preparing metal alcoholates and organometallic compounds soluble in organic solvents by  
electrolysis of a metal material in an alcohol in the presence of an electroconductive additive;

said metal alcoholates comprise alcoholates of a metal selected from the group consisting of Mg, Al, Ga, In, Y, La, Ce, Ti, Zr, Hf, Nb, Ta, Fe, Co, Ni, Ca, Se, Pr, Sm, Si, Te, Yb, Sn, Pb, V, Nd, Gd, Tb, and Sc;

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said organic solvents comprise at least one

solvent selected from the group consisting of an enamel solvent, gasoline, petroleum ether, naphtha, benzene, toluene, acetone, hexane, ethylcellosolve, and isopropanol; and

5                   said electroconductive additive comprises water vapor in a gas selected from the group consisting of air and an inert gas.

10                   16. A process in accordance with claim 15 wherein said metal material is selected from the group consisting of: a metal alkoxide, an organometallic precursor, a metal alloy, and a metal compound, and elemental metal.

15                   17. A process in accordance with claim 15 wherein said electrolysis comprises electrode dissolution by AC current, DC current, or combinations thereof.

18. A process for preparing composite ceramics, comprising the steps of:

20                   forming a substantially homogeneous region of metal alcoholates and organometallic compounds on a substrate to produce composite ceramics by

25                   coating electrochemically prepared metal alcoholates and organometallic compound soluble in organic solvents on said substrate,

hydrolyzing said alcoholates to oxides and alcohols,

heating and vaporizing said organic solvents,

30                   sintering or annealing said metal oxides, said metal alcoholates comprise alcoholates of a metal selected from the group consisting of: Mg, Al, Ga, In, Y, La, Ti, Zr, Hf, Nb, Ta, Fe, Co, Ni, Ca, Se, Pr, Ce, Sm, Si, Te, Yb, Sn, Pb, V, Nd, Gd, Tb, and Sc; and

35                   said organic solvents comprise at least one solvent selected from the group consisting of an enamel solvent, gasoline, petroleum ether, naphtha, benzene,

toluene, acetone, hexane, ethylcellosolve, and isopropanol.

19. A process in accordance with claim 18 wherein said substrate comprises a metal.

5

20. A process in accordance with claim 18 wherein said substrate is selected from the group consisting of: an optical lens, a catalyst, ball bearings, a turbojet, a combustion engine, chemical equipment, pipelines, aerospace components, a piston, a cylinder, automobile parts, high temperature apparatus, tools, dental coatings, teeth, a semiconductor, and superconductive material.

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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US94/13707

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C25B 3/12; B05D 3/02

US CL : 204/59QM; 427/226, 126.3; 205/195, 196, 224

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 204/59QM; 427/226, 126.3; 205/195, 196, 224

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS ("alcoholates", "electrode dissolution", "hydrolyz7", "alkoxide")

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,137,749, (Yamazaki et al) 11 August 1992 (see col. 1, lines 11-19 and col. 2, line 50 through col. 3, line 1)	1-20
Y	US, A, 5,132,253 (Dawes) 21 July 1992 (see col. 1, lines 1-16 and col. 3, lines 30-49)	1-20
Y	SU, 095,3008 (Heteroorgan CPDS) 23 August 1982 (see Abstract)	1-20
A	US, A, 3,964,983 (Eisenbach et al) 22 June 1976 (see whole document)	1-20

☒ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means		
*P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

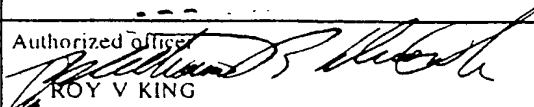
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**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/US94/13707

**C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A, 4,250,000 (Kuck et al) 10 February 1981 (see whole document)	1-20
A	US,A, 4,853,207 (Wautier et al) 01 August 1989 (see whole document)	1-20